REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

0067

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1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
6/15/01	FINAL	3/1/1999 - 2/28/2001

4. TITLE AND SUBTITLE
Bonding, Energetics and Mechanical Properties of Intermetallics

5. FUNDING NUMBERS
F49620-98-1-0321

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Scientific Research (AFOSR)
801 N. Randolph Street, Room 732
Arlington, VA 22203-1977

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for public release, unlimited distribution

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

To fulfill the great potential of intermetallic alloys for use in high temperature structural applications, it is necessary to understand on the microscopic level the mechanisms controlling their mechanical behavior, including such key phenomena as dislocation structure and mobility, crack blunting and propagation, the role and the effect of alloying additions: while they have been characterized by mesoscopic length and energy scales, they are determined on the microscopic level by the electronic structure.

20030319 072

14. SUBJECT TERMS

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
U	U	U	

97-NA-393

BONDING, ENERGETICS AND MECHANICAL PROPERTIES OF INTERMETALLICS.

AFOSR GRANT No. F49620-98-1-0321

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Abstract

To fulfill the great potential of intermetallic alloys for use in high temperature structural applications, it is necessary to understand on the microscopic level the mechanisms controlling their mechanical behavior, including such key phenomena as dislocation structure and mobility, crack blunting and propagation, the role and the effect of alloying additions: while they have been characterized by mesoscopic length and energy scales, they are determined on the microscopic level by the electronic structure.

Objectives

The objective of this research is to investigate fundamental aspects of the fracture and deformation behavior of ordered intermetallic aerospace alloys on the basis of the ab-initio determination of the parameters needed for further (i) model theoretical, (ii) band structure and (iii) chemical bonding analyses. The research is targeted at investigating the microscopic mechanisms governing the deformation and fracture behavior of intermetallic alloys in order to contribute to the development of a fundamental basis for computer-aided alloys design. The most important and challenging component of our research is to bridge the gap between a microscopic quantum-mechanical description of the chemical bonding and the mesoscopic phenomena which govern the mechanical response of intermetallics. The emphasis on the computational/simulation approach focuses on understanding "real" materials, which have an abundance of "defects" including impurities and vacancies, dislocations or other faults, second phase precipitates, etc. - all of which are governed on the microscopic level by the electronic structure.

Basic research issues and approach

We concentrate on the following key problems specifically for intermetallic compounds and metals of interest: (i) dislocation structure and mobility; (ii) dislocation core structure in $L1_2$ intermetallics in the context of understanding their anomalous mechanical response; (iii) features of electronic structure of dislocations and their interaction with point defects; (iv) alloying effect on plasticity and phase stability. These important, complex problems require the use of a hierarchy of methods. Thus, we focus on the application and further development of both state-of-the-art band structure and real-space large scale cluster electronic structure methods, and our recently developed 2D Peierls-Nabarro model, which we have combined into a novel "continuum/atomistic" description. This approach allows to treat the mesoscale nature of dislocations in a most natural way and to provide a physically transparent description of dislocation structure that is suitable for use with larger length scale modeling. As demonstrated below, this combined ab-initio-model approach led to dramatic clarification of some important questions in the area of the materials science of intermetallics.

Recent research findings

1. Superdislocation core structure in $L1_2$ Ni_3Al, Ni_3Ge and Fe_3Ge via an ab-initio GSF-Peierls-Nabarro approach.

It is now well established that yield stress anomaly (YSA) is the intrinsic property of most $L1_2$ intermetallics originating in the structure and properties of superdislocations. The quasi-binary system Ni_3Ge-Fe_3Ge is an interesting example of a gradual transition from anomalous to normal behavior as Fe is substituted for Ni. Recently, state of the art HREM measurements of the stacking fault separations in Fe_3Ge-Ni_3Ge did not allow establishing a convincing correlation between core structure and the absence of YSA at some Fe concentrations [1]. Thus, due to lack of experimental information and limitations of atomistic simulations with model interatomic potentials, it remains unclear what mechanism and factors predetermine the absence of the YSA in a few $L1_2$ intermetallics.

We employed our combined theoretical approach based on ab-initio total energy and interatomic force calculations with microscopic information used for larger scale modeling within the Peierls-Nabarro (PN) model. We used an accurate band structure methodology to calculate generalized stacking fault (GSF) energetics (γ-surface) to relate this microscopic characteristic with dislocation properties. In contrast with the original PN model we consider its two dimensional (2D-PN) generalization with a discrete representation of the misfit energy and find solutions of this modified PN model within the class of analytic functions [2].

In order to determine the GSF surface energetics, the local-density approximation (LDA) and the full-potential linear muffin-tin orbital (FLMTO) method were employed. Constrained atomic relaxations along the direction perpendicular to the {111} slip plane have been taken into account. A regular mesh sampling was used to fit the entire GSF to determine positions of the local minimum and energies of the corresponding stacking faults (APB, CSF and SISF) for the binary Ni_3Al, Ni_3Ge and Fe_3Ge. The results are presented in Table 1 and contain energy values determined for both the stacking fault vectors according to geometrical considerations, and vectors corresponding to the local minima of the ab-initio GSF surface.

Table 1: Stacking fault energies (mJ/m^2), calculated from geometrical fault vectors (geom.) and from vectors corresponding to the position of the local minimum on GSF surfaces (min.).

Alloy	γ_{APB}		γ_{CSF}		γ_{SISF}
	geom.	min.	geom.	min.	
Ni_3Al	270	210	290	225	80
Ni_3Ge	660	550	620	no	420
Fe_3Ge	330	no	315	no	17

The complex character of interatomic interactions in $L1_2$ alloys causes the GSF surface geometry to differ significantly from what is usually anticipated on the basis of a hard-sphere model. In particular, as seen in Fig.1, a GSF minimum corresponding to a CSF does not exist in either Ni_3Ge or Fe_3Ge, and an APB minimum on the {111} plane does not exist in Fe_3Ge. Moreover, the position of the existing APB minimum is noticeably shifted from its geometrical counterpart, resulting in an appreciable renormalization of the energy in Ni_3Al

and Ni_3Ge (see Table 2).

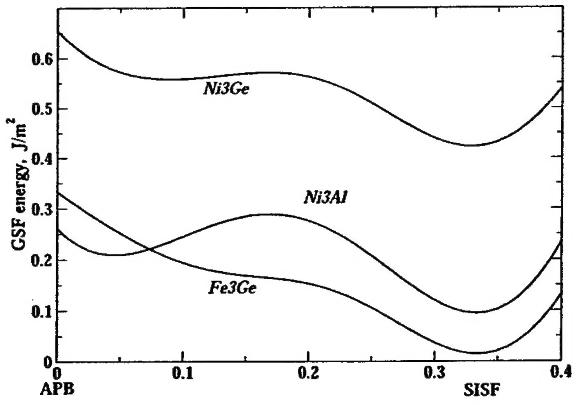

Figure 1: GSF sections for the select direction, which correspond to the path from APB (geom.) to SISF positions in the <112> direction.

Table 2 presents theoretical values of the separation between superpartials, d_{APB} and Shockley partials (d_{CSF}), calculated within continuum elasticity and using the extended 2D-PN model. Since not all of the stacking faults exist (see the min energy values in Table 1), the corresponding separation distances cannot be determined within the continuum elasticity framework. The 2D-PN model, however, allows the complete determination of dislocation core structure without assumptions regarding the splitting scheme or the number of partial dislocations [2]. It is interesting that in Ni_3Al we found several stable solutions (two of them are shown in Fig. 2(a)) and that switching between them may take place during dislocation motion.

Table 2: Partials separation calculated for screw type I superdislocation. Elasticity theory estimates of partials separation given both for geometrical and stacking fault energies determined as the local minimum of the ab-initio GSF (see Table 1).

Alloy	d_{APB}				d_{CSF}		
	elasticity		2D-PN	exp.	elasticity		2D-PN
	geom.	min.			geom.	min.	
Ni_3Al	3.21	4.13	3.5 – 5.2	~ 4.3	0.68	0.53	0.8 – 0.95
Ni_3Ge	1.38	1.65	1.7	~ 2.4	0.4	no	0.4

The advantage of an appropriate 2D-PN model analysis over continuum elasticity theory becomes evident in the analysis of Fe_3Ge. In this case, it is predicted that a stable solution for the four-fold splitting scheme (type I) does not exist, despite the fact that the APB energy in the geometrical point is not very different from Ni_3Al. In the case of Fe_3Ge, the only stable solution is a superdislocation with type II core structure, which corresponds to the Kear splitting scheme with a SISF band. The microscopic reason for this is connected to peculiarities of the γ-surface, namely, the APB-minima in Fe_3Ge is absent (Fig. 1)

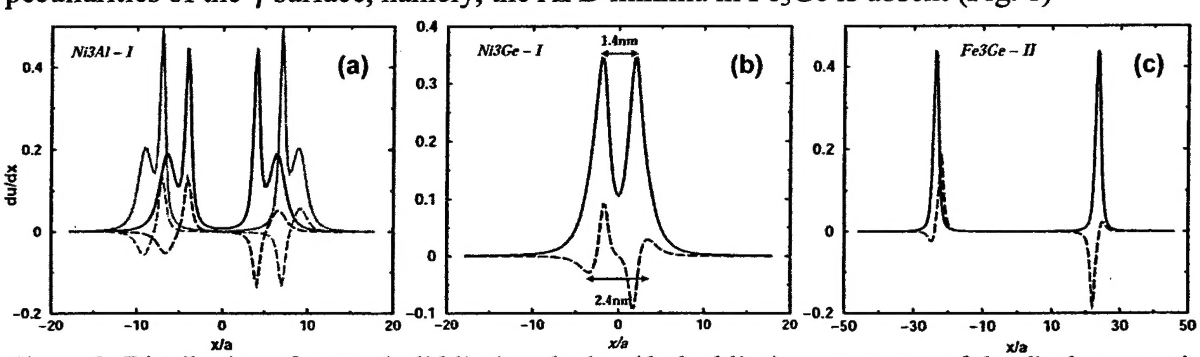

Figure 2: Distribution of screw (solid line) and edge (dashed line) components of the displacement in core type I superdislocations for Ni3Al (a), Ni3Ge (b) and in type II superdislocations for Fe_3Ge (c).

Thus, our results indicate that our modeling approach describes adequately the equilibrium

core structure in these complex compounds. We predicted that two types of superdislocations are possible in Ni_3Al and only the type I superdislocation in Ni_3Ge. Indeed, types I and II were observed in Ni_3Al at low temperature, and there is no experimental evidence of a type II superdislocation in Ni_3Ge. The Fe_3Ge presents the opposite case; type I superdislocations do not exist and only type II may be realized in a stable configuration. We believe that the disappearance of type I superdislocations, because of an unstable APB energy, is the main reason for the lack of a yield stress temperature anomaly in Fe_3Ge.

2. Energetics and mechanism of impurity-dislocation interactions in NiAl.

The improvement of the strength of materials due to doping by ternary additions has become a traditional alloy design approach. According to the prevailing point of view [1], the size misfit between the impurity and host atoms appears to make the main contribution in impurity-dislocation interaction and solid solution hardening (SSH) in a majority of alloys. In NiAl [4], however, SSH differs significantly for elements with similar atomic radii: it is very high for early 3d, 4d and 5d elements ("extra" SSH), but low for B-subgroup elements. To understand the nature of these differences, the energetics of the interaction of the <100>{010} edge dislocation in NiAl with different kinds of impurities (Ti, V, Cr, Mn, Zr, Mo, Si, Ge and Ga) was studied using the ab initio real-space tight-binding LMTO-recursion method (TB-LMTO-REC) [5]. 20,000 atom clusters were used with up to 1,000 non-equivalent atoms in the dislocation core. The coordinates of the atoms in the core were determined within the Peierls-Nabarro (PN) model with restoring forces determined from full-potential LMTO total energy calculations [6].

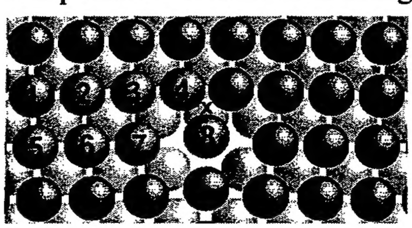

Figure 3: Fragment of the model of the central part of the (100){010} edge dislocation in NiAl; Ni and Al atoms are represented by light and dark spheres, respectively, and substitution impurity positions are marked 1-8; "X" marks the central Ni atom of the core.

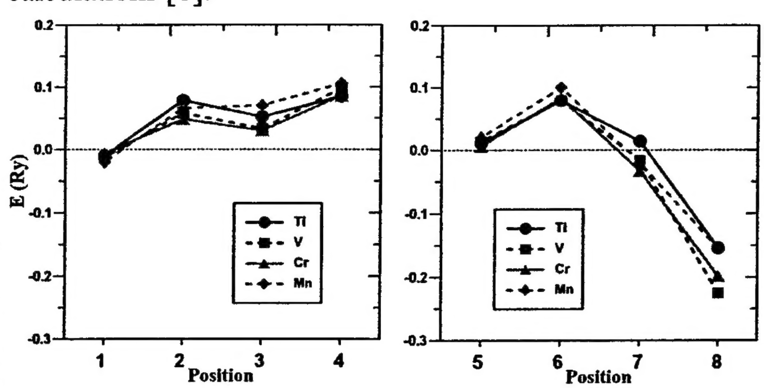

Figure 4: Impurity-dislocation interaction energy for 3d-impurities in positions: (a) 1-4; (b) 5-8.

The impurities were placed in positions (1-8) near the <100>{010} edge dislocation core in NiAl (Fig. 3), substituting the corresponding Al atom. For all early 3d-metal impurities the impurity dislocation interactions is similar to the previously reported behavior for Ti and V (Fig. 4). For most impurity positions (1-7), "repulsion" between the dislocation and impurity takes place, which will lead to a "friction" effect during the dislocation glide. However, the impurity-dislocation interaction becomes strongly attractive for an impurity in position 8, causing a "chemical locking". An analysis of the local electronic structure in the dislocation core reveals that the nature of the locking is due to the strong hybridization and preferred bonding between the electronic states of the impurity atom and the localized electronic states forming in the center of the dislocation core. The resulting decrease of the one-electron

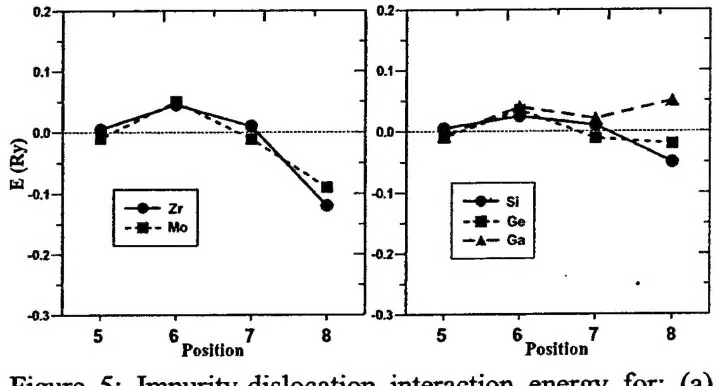

Figure 5: Impurity-dislocation interaction energy for: (a) 4d-elements, (b) B-subgroup elements in positions 5-8.

energy becomes the main contribution to the impurity-dislocation interaction energy.

One may expect that similar impurity-dislocation interaction mechanisms will also take place in NiAl doped with early 4d and 5d impurities since these elements are electronic analogues of the early 3d elements. We performed the calculation of the impurity-dislocation interactions for 4d elements Zr and Mo (Fig. 5(a)). Similar to 3d elements, the interaction ranges from repulsive (for impurities in positions 1-7) to attractive for impurities in position 8, due to the strong interaction of impurity states with localized states on the dislocation. These results demonstrate that electronic mechanisms rather than the size misfit mechanism are respon-sible for the extremely potent SSH effect of early 3d, 4d and 5d impurity elements [4,7].

The energetics of interaction of B-subgroup elements Si, Ge and Ga with the <100>{010} edge dislocation in NiAl (Fig. 5(b)), however, is significantly different from those of d-elements: the interaction energy is lower for all positions; for impurities in position 8 it is only weakly attractive for Si and Ge and even repulsive for Ga. Therefore, the electronic contribution to the impurity-dislocation energy will be small, and the impurity-dislocation interaction can be controlled by the elastic mechanism.

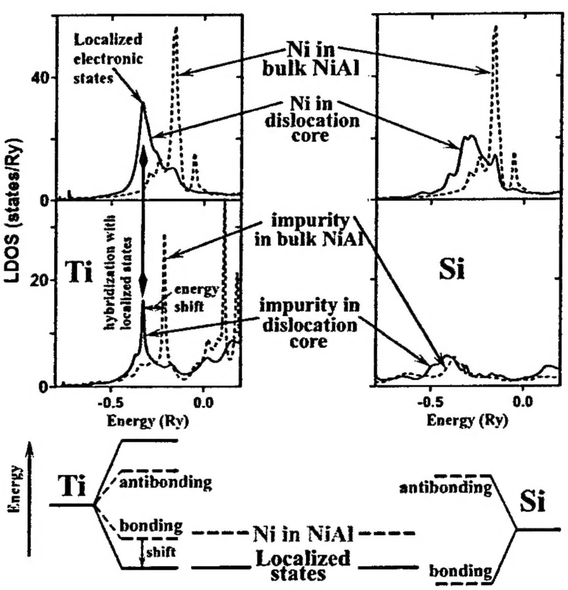

Figure 6: LDOS for Ti and Si impurities in bulk NiAl and in position 8 near the dislocation core and a schematic energy-level diagram.

An energy-level diagram schematically representing the interaction of impurity electronic states with localized states in the core of the <100>{010} edge dislocation is shown in Fig. 6 for Ti and Si, taken as representative examples. When the impurity atom is introduced into the bulk host material, its electronic states split into bonding and antibonding states as a result of hybridization with electronic states of the host. When the impurity atom is placed near the center of the dislocation core, its bonding states hybridize with localized states of the dislocation core. If bonding states of the impurity in the bulk material are located energetically higher than the localized dislocation states (as in Ti), their hybridization with localized dislocation states will lead to an additional lowering of the bonding states, an increase of the splitting between bonding and antibonding states, and a negative one-electron contribution to the impurity-dislocation interaction energy. If bonding states of the impurity are located at the

same position or lower than the dislocation localized states (as in Si), their interaction will be weak and will give no additional contributions to the impurity-dislocation interaction energy.

Thus, this analysis shows that based on electronic structure calculations of the impurity in the bulk material, it is possible not only to explain the "extra" SSH effect, but also to predict how the impurity atom will interact with the dislocation core and to estimate the electronic contribution to the impurity-dislocation interaction energy.

3. Effect of rhenium on the electronic structure and mechanical properties Cr-Re alloys. The microscopic mechanism of the "rhenium effect".

Chromium and Cr -based alloys are attractive materials for high temperature application due to low density, high creep strength and good oxidation resistance [8]. Recently, an additional interest appeared in context of the development of dual-phase alloys based on Cr solid solution reinforced Cr_2X (X= Nb, Te, Zr) Laves phases [9]. Unfortunately, chromium is brittle at room temperature. As was established for the VI-A group metals (Cr, Mo, W), the addition of Re at concentrations close to the solubility boundary significantly improves the mechanical properties, mainly due to the lowering of the ductile-brittle transition temperature and the increase strength (so called "rhenium effect" [8]). However, the lack of understanding on the fundamental level of mechanisms controlling the changes of ductility and strength due to Re additions seems to be a large obstacle in the search for new commercial alloys with better mechanical properties.

The electronic structure and ground state characteristics of Cr-Re alloys in a wide range of Re concentration were investigated using the full-potential LMTO method with LDA and GGA. The ground state parameters obtained for pure Cr (equilibrium lattice parameters a, bulk modulus B and tetragonal shear modulus C' and cohesive energies are in good agreement with available experimental data.

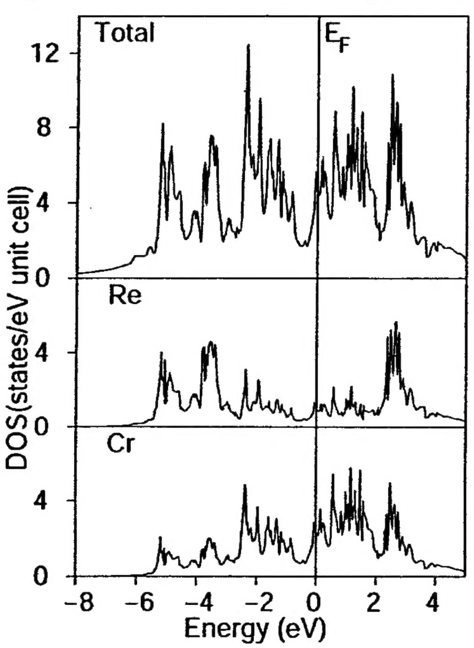

Figure 7: DOS for A15 Cr_3Re.

Table 3: Cohesive energy (Ry/atom) of the bcc Cr and Cr-25% Re, A15 Cr_3Re and Cr_3Re-C, and bcc Cr with C.

Cr	Cr-25Re	A15 Cr_3Re	Cr_6Re_2C	Cr-C
0.69	0.73	0.68	0.78	0.73

To understand the microscopic mechanisms of the "rhenium effect", we investigated the existence of the Cr_3Re close-packed phase with A15 structure. We found that it has a similar electronic structure with that of bcc Cr alloyed with the same Re concentration (25 at.% Re). We optimized the crystal parameters of hypothetical A15 Cr_3Re compound and found that the density of states, the location of E_F and value of the cohesive energies (Table 3) are similar for the Cr-25 at.% Re alloy and the A15 Cr_3Re phase. This phase would be rather unstable because E_F falls at the high peak in the DOS (Fig. 7). We found that A15 Cr_3Re may be stabilized by deviations from stoichiometry or

by interstitial impurities.

We also investigated the A15 Cr_3Re with additions of carbon at the tetrahedral interstitial site by considering a Cr_6Re_2C supercell. As one can see from Table 3, the carbon interstitial impurities may be effective for stabilizing A15 Cr_3Re particles. Apart from this, A15-like precipitates may be rather favorable compared with the brittle carbide or oxide particles

The prediction of A15-like clusters provides support to a of the nature of rhenium effect [8] based on the assumption about the key role of Me-Re close-packed particles in the phase equilibrium of alloy. First of all, the precipitation of these clusters may substantially change the phase and structural state of the alloy. In particular, interstitial impurities may be scavenged into the A15-like regions. Because of small size and good conjugation with the matrix, these A15 precipitates are helpful for ductility. Secondly, there will be solid solution or precipitation hardening from these clusters/precipitates. Hence, we believe that understanding the mechanism of precipitate formation in Cr - Re alloys may allow one to find new chromium alloys with desirable properties.

Future Plans

Our future plans include investigations of:

1) Fundamental aspects of dislocation properties and deformation behavior: dislocation structures in homogeneous phases and with intrinsic interfaces: (i) $L1_2$ Ni_3Al and $(Ni_{1-x}Fe)_3Ge$; (ii) comparison with HREM images; (iii) multiple core dislocation structures in intermetallics; (iv) incoherent misfit strain: properties of the misfit dislocations.
2) Effect of alloying on the properties of intermetallics: (i) intrinsic interfaces (APB, CSF, and SISF) in NiAl and Ni_3Al; (ii) direct total energy calculations of dislocation-impurity interactions.
3) Fundamentals of the electronic structure of dislocations: (i) glide of dislocations; (ii) complex dislocation structures (kinks, jogs), (iii) transport properties.
4) Effect of intrinsic interfaces on fundamental characteristics of mechanical behavior of eutectic composites and coherent two-phase structures: (i) NiAl/X eutectic composites (X = Mo, W, Cr, Re and V); (ii) γ/γ' superalloys NiX-Ni_3AlX (X = Ti, V, Cr, Co, Zr, Re, Ir).

Acknowledgement/Disclaimer

This work was supported by the Air Force Office of Scientific Research, USAF, under grant number F49620-98-1-0321 and computer time grants at NSCA, SDSC, NAVO and ARL. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

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